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Cooperative Catalysis

A Pd–H/Isothiourea Cooperative Catalysis Approach to *anti*-Aldol Motifs: Enantioselective α-Alkylation of Esters with Oxyallenes**

*Hua-Chen Lin, Gary J. Knox, Colin M. Pearson, Chao Yang, Veronica Carta, and Thomas N. Snaddon**
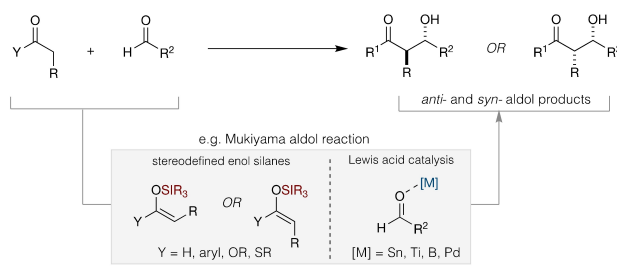
Dedicated to Dr. Hendrik Helmke

Abstract: The biological and therapeutic significance of natural products is a powerful impetus for the development of efficient methods to facilitate their construction. Accordingly, and reflecting the prevalence of β-oxy-carbonyl motifs, a sophisticated arsenal of aldol-based strategies has evolved that is contingent on the generation of single enolate isomers. Since this has the potential to compromise efficiency in reagent-based paradigms, direct catalysis-based solutions would be enabling. To complement the array of substrate-based strategies, and regulate enolate geometry at the catalyst level, a direct catalytic alkylation of esters with oxy-allenes has been developed. Synergizing metal hydride reactivity with Lewis base catalysis has resulted in a broad reaction scope with useful levels of stereocontrol (up to >99% *ee*). Facile derivatization of these ambiphilic linchpins is demonstrated, providing access to high-value *vicinal* stereocenter-containing motifs, including 1,2-amino alcohols.

Metal hydrides (M–H) manifest themselves in all facets of the contemporary catalysis spectrum.[1] The success of these intermediates reflects their versatile reactivity profile which, in turn, can be modulated through judicious choice of the metal and/or the supporting ligands. Despite the steep trajectory of advances in this arena, strategically leveraging π-bond activation by M–H species in conjunction with Lewis base catalysis within the framework of enantioselective cooperative catalysis remains conspicuously under-developed.[2] Our interest in combining transition metal- and Lewis base organocatalysis[3–5] presented an opportunity to reconcile this disparity and in so doing unveil new avenues to expedite th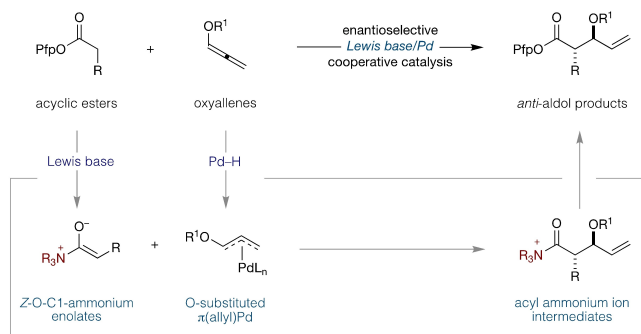e synthesis of motifs that are common to an array of bioactive molecules such as polyketides. Established aldol preparations typically proceed via the same general template in which enolates (or enolate equivalents) react with aldehyde electrophiles (Figure 1a).[6] Based on this a range of Mukaiyama-type aldol reactions catalyzed by Lewis acids are now available.[7] While these continue to be exceptionally successful, approaches that avoid the trapping of carbonyl electrophiles by independently and selectively prepared stereodefined enolates have emerged.[8] Cognizant of these challenges, we envisioned the preparation of enantioenriched aldol products via the *direct* enantioselective alkylation of acyclic esters with oxyallenes[9] in a manner that is complementary to established approaches and facilitates access to high value ambiphilic C5 linchpins that can be functionalized in a bidirectional manner (Figure 1b).

We envisioned a cooperative isothiourea Lewis base–Pd catalyzed process that proceeds via the stereoselective union

[*] Dr. H.-C. Lin, Dr. G. J. Knox, Dr. C. M. Pearson, Dr. C. Yang,
Dr. V. Carta, Dr. T. N. Snaddon
Department of Chemistry, Indiana University
800 East Kirkwood Avenue, Bloomington, IN 47405 (USA)
E-mail: tsnaddon@indiana.edu

Dr. H.-C. Lin
Current address: School of Chemistry and Chemical Engineering
Jiangsu University, Zhenjiang, 212013 (P. R. China)

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Figure 1. a) General depiction of aldol construction. b) This work: enantioselective alkylation of acyclic esters with oxyallenes via cooperative catalysis.

of (Z)-O–C1-ammonium enolate and O-substituted π(allyl)-Pd intermediates (Figure 1b), wherein the requisite O-substituted π(allyl)Pd species would arise by hydropalladation of the oxyallene by a transient hydrido-palladium (Pd–H). If successful, such a scenario would address the issue of enolate geometry and proceed via a non-enolizable electrophilic species. In support of this proposal, the Pd-catalyzed alkylation of a limited range of carbon nucleophiles with alkoxyallenes, which proceed via putative Pd–H intermediates, have been reported.[10]

As an entry point for our investigation, we began by evaluating the alkylation of pentafluorophenyl (Pfp) ester **1** with benzyloxyallene **2a** in THF and in the presence of both benzotetramisole **LB1**,[11,12] [Pd-OMs]$_2$ and Xantphos (**L1**) (Table 1). The O-benzyl aldol product **3** was obtained in 80% yield as the *anti*-diastereoisomer (2.5:1 dr) in 98:2 er (Entry 1). The corresponding linear product **4** was barely detectable with the remainder of the mass balance comprising mixed acetal **5**, which was obtained in 13% yield. We presumed this to arise from attack of liberated pentafluophenolate upon a likely π(allyl)Pd$^+$ intermediate.[13] We then moved to evaluate the effect of solvent on both the efficiency and stereoselectivity of the reaction (Entries 2–6) which revealed that formation of competing hemi-acetal byproduct **5** was minimized in toluene.

Thereafter, and cognizant of the critical effect that bis-phosphine ligand parameters have on both Pd–H reactivity and hydricity,[1b,14] as well as the reactivity, regioselectivity and *syn/anti* population of π(allyl)Pd species, we sought to evaluate the effect of the supporting ligand on palladium. Accordingly, we evaluated common bis-phosphine ligands in order of decreasing natural bite angle.[15] DPEphos **L2** (Entry 17, 104°) and DPPF **L3** (Entry 8, 99°) resulted in the same high yields and enantioselectivities but with increased diastereoselectivity (3.2:1 dr and 3.6:1 dr, respectively); however, BINAP **L4** was ineffective[16] (Entry 9, 93°), as were the smaller bite angle aliphatic bisphosphines DPPP **L5** (91°) and DPPE **L6** (86°) (Entries 10 and 11, respectively). Finally, we also surveyed Trost's chiral bidentate DACH-Ph **L7**, a privileged ligand in Pd-catalyzed allylic alkylation,[17] but this was also ineffective (Entry 12).[16] Finally, common monophosphine ligands were similarly ineffective and did not result in active catalysts (see Supporting Information). Having completed our ligand assessment and having identified dppf as the most effective, we then confirmed the identical performance of Buchwald's stable and convenient 3rd generation pre-catalyst **G3L3**,[18] which we used subsequently (Entry 13). We then evaluated three other common isothiourea Lewis base catalysts (**LB2**–**LB4**, Entries 14–16) in combination with **G3L3**; however, none outperformed BTM **LB1** (Entry 13). At this juncture and based on our previous observations in isothiourea/palladium catalysis, we expected that the observed diastereoselectivity (ca. 3.6:1, *anti/syn*, Entry 13) derived from C1-ammonium enolate alkylation by isomeric *syn*- and *anti*-π(allyl)Pd intermediates.[5d,e] As, in addition to ligand effects, both substrate steric and electronic factors have been observed to influence the relative populations of these two isomers,[19] we elected to evaluate and compare phenoxyal-

Table 1: Reaction development and optimization.

Entry[a]	oxyallene	Lewis base	Ligand (bite angle)	Solvent	Yield 3 [%][b]	dr[c]	ee [%][d]
1	**2a**	LB1	L1 (108°)	THF	80 (13)	2.5:1	94
2				Et$_2$O	70 (16)	2.3:1	81
3				1,4-dioxane	53 (9)	2.3:1	96
4				PhCH$_3$	87 (4)	2.5:1	96
5				CH$_2$Cl$_2$	77 (13)	1.2:1	48
6				MeCN	79 (11)	1.1:1	30
7			L2 (104°)	PhCH$_3$	86 (7)	3.2:1	97
8			L3 (99°)		86 (6)	3.6:1	96
9			(R)- or (S)-L4 (93°)		--	--	--
10			L5 (91°)		--	--	--
11			L6 (86°)		--	--	--
12			(R,R)- or (S,S)-L7		--	--	--
13			G3L3		86 (6)	3.6:1	96
14[e]		LB2			21 (13)	2.0:1	−85
15		LB3			83 (15)	3.4:1	88
16		LB4			87 (8)	1.3:1	20
17	**2b**	LB1			90	9.5:1	99

[a] Reactions performed on a 0.1 mmol scale. [b] ^{1}H NMR yield calculated using 1,2,4,5-tetramethylbenzene as an internal standard. Yields in parentheses refers to mixed acetal **5**. [c] Diastereoisomer ratio calculated by comparison of relevant peak integrals in crude ^{1}H NMR spectrum. [d] Determined by HPLC analysis on a chiral stationary phase. [e] 30 mol% iPr$_2$NEt was added. Bn = benzyl, OMs = methane sulfonyl, Pfp = pentafluorophenyl.

lene **2b** as we expected increased conjugation and/or increased steric discrimination in the intermediate OPh-substituted π(allyl)Pd$^+$ intermediate would result in increased product *anti*-diastereoselectivity. Indeed, phenoxyallene **2b** gave aldol product **3b** in 90% yield and much improved 9.5:1 dr without compromising the level of enantioselectivity.

With optimized conditions established and having identified the critical influence of the O-substituent on the diastereoselectivity of the alkylation reaction, we next moved to evaluate the scope of the oxyallene partner more widely. As shown in Scheme 1, various aryloxyallenes
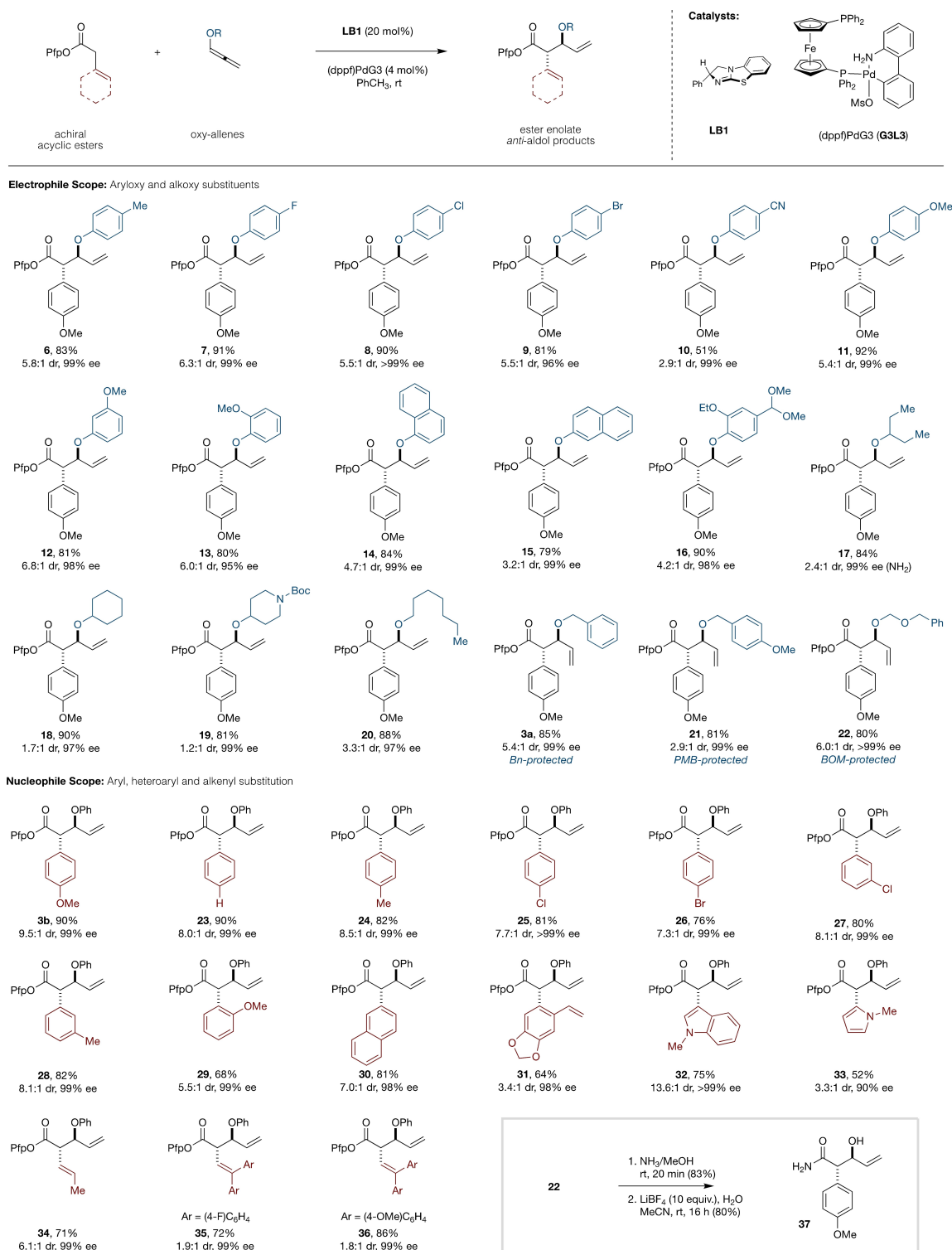
Scheme 1. Ester and oxyallene substrate scope.

reacted with ester **1** under the optimized conditions and provided *anti*-aldol products in high yields, with excellent levels of enantiocontrol and with good levels of diastereose-lectivity. There appears to be little sensitivity to changes in the electronics of the arene; in addition to simple methyl substitution (**6**), fluoro (**7**), chloro (**8**) and bromo (**9**)
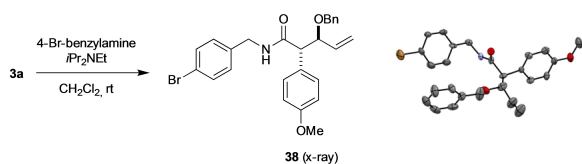
substituents are all tolerated and remain unaltered during the reaction. Comparing electron-withdrawing and electron-donating substituents via *p*-nitrile (**10**) and *p*-methoxy (**11**), respectively, indicated that the former functions with slightly lower levels of efficiency and diastereocontrol. We then interrogated both the electronic and steric effect of the

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methoxy substituents via the corresponding *m*-methoxy (**12**) and *o*-methoxy (**13**) isomers, which participated with slightly enhanced levels of diastereocontrol. In the case of isomeric and 1- and 2-naphthyloxyallenes (**14** and **15**, respectively) both reacted in similar yield but with enhanced levels of diastereocontrol in the case of **14**. Finally, more complex acetal-containing aryloxyallene gave **16** in with comparable efficiency. Thereafter, we proceeded to evaluate the scope of alkoxyallenes; both acyclic and cyclic aliphatic substitutes gave alkylated products in high yields and enantioselectivities, albeit with lower levels of diastereocontrol relative to the aryloxyallenes. Acyclic alkyl allenyl ethers (**17** and **20**) gave higher levels of *anti*-selectivtiy than the corresponding cyclic cyclohexyl and *N*-Boc piperidinyl congeners (**18** and **19**, respectively).

Finally, we established that PMB (**21**) and BOM-protected (**22**) products could be produced that, in combination with Bn-protected product (**3a**), provide complementary opportunities for downstream deprotection. Noteworthy is the continued tolerance toward halides (**25–27**), as well as tolerance of *o*-substituted arenes (**29** and **31**), indole (**32**), pyrrole (**33**), and alkenyl substrates (**34–36**). Having established the utility of oxyallenes bearing various protecting groups, we then sought to demonstrate access to "free" aldol products. BOM-Protected aldol product **22** was first subjected to ester ammonolysis before BOM-deprotection **37**.

The absolute and relative stereochemical features of the products were confirmed via single-crystal X-ray analysis of **38**,[20] the *p*-Br-benzylamide of **3a**, which crystallizes in the rare space group *P*1 with four symmetry-independent molecules in the asymmetric unit (*Z*′ = 4) (Scheme 2). Further information concerning the structural characterization of compound **38** is available in the Supporting Information.

Having assessed the scope of this enantioselective alkylation and secured the relative and absolute stereochemistry of the major isomers through single crystal analysis, we then sought to demonstrate the utility of the product esters. We recognized the synthetic potential the Pfp ester as a handle to prepare synthetically valuable 1,2-amino alcohols[21] as we have previously described that α-branched Pfp esters react instantaneously with gaseous ammonia to give the corresponding primary amides, which then undergo efficient stereoretentive rearrangement upon treatment with an appropriate oxidant.[5b] As a preliminary validation of this, alkylation of six arylacetic acid Pfp esters with two phenoxyallenes followed by ammonolysis produced the α-aryl-β-aryloxy primary amides. Following trivial separation, the amides were converted via Hofmann rearrange-

ment to the corresponding diastereomerically and enantiomerically pure *N*-carbamoyl-1,2-amino alcohols (**39–44**) in good overall yield (Scheme 3).

From a mechanistic perspective two aspects of this reaction warrant closer scrutiny: 1) in contrast to established precedent,[5] no exogenous base is required to generate the ammonium enolate via enolization,[22] and 2) no exogenous Brønsted acid is required to generate the putative Pd–H intermediate necessary for oxyallene hydropalladation.[9] To gain insight into these two facets, we employed α,α-deuterium enriched **1**-D$_2$ in the alkylation with phenoxyallene **2b** (Scheme 4, top). We established that one of the
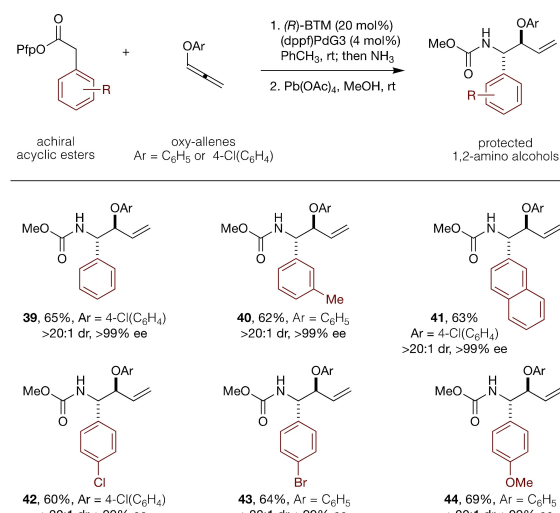
Scheme 3. Conversion to 1,2-amino alcohols.
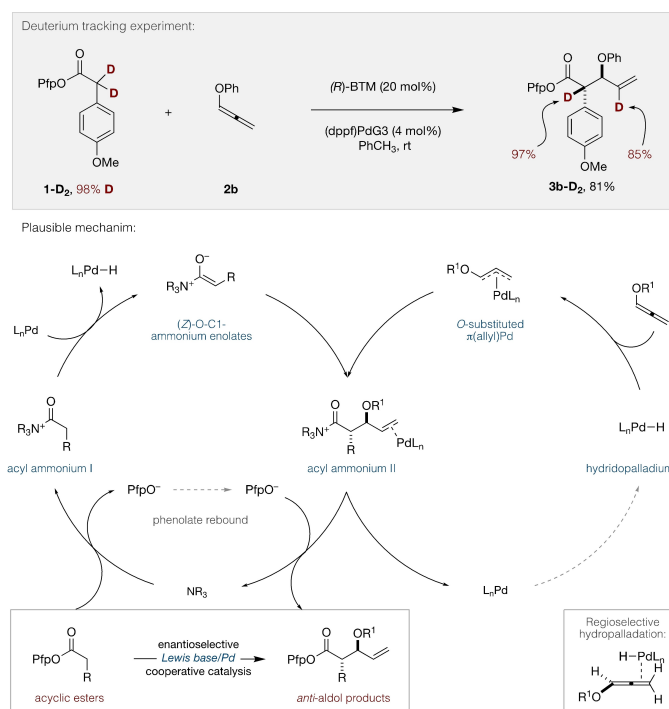
Scheme 4. Deuterium tracking and proposed mechanism.

Scheme 2. Preparation and X-ray analysis of **38**.

deuterium atoms is incorporated *only* at the central carbon of the phenoxyallene (85 %) while the other deuterium is fully retained (97 %). The fidelity of this deuteron-transfer, and the fact that no product is formed in the absence of either catalyst, suggests that the requisite Pd–D is formed directly from an acylammonium ion intermediate. This unveils a further cooperative aspect to this transformation where, in addition to playing a critical role in the key carbon-carbon bond forming event, the Pd catalyst is involved in the formation of both C1-ammonium enolate and RO-substituted π(allyl)Pd$^+$ species.

A plausible mechanism is presented in Scheme 4, bottom: reaction of the Pfp acyclic ester with the isothiourea catalyst (NR$_3$) liberates PfpO$^-$ and gives acylammonium ion I, which upon interception by Pd affords the corresponding (*Z*)-O–C1-ammonium enolate and Pd–H. Thereafter, regioselective hydropalladation of the terminal π-bond of the oxyallene by Pd–H results in O-substituted π(allyl)Pd,[23] which is intercepted by the ammonium enolate. Thereafter, decomplexation of Pd and turnover of the isothiourea via PfpO$^-$ rebound[5i,24,25] provides enantioenriched aldol products.

In summary, we have developed an enantioselective alkylation of acyclic esters with oxyallenes that is catalyzed by a cooperative isothiourea and palladium catalyst system. The reaction displays broad generality and provides direct access to useful O-substituted aldol products that would be challenging to access via alkylation/arylation of parent aldol scaffolds due to competing retro-aldol fragmentation. The further utility of the Pfp ester-containing products is also demonstrated via conversion to valuable 1,2-amino alcohols. Finally, preliminary mechanistic investigation has revealed the manner of hydridopalladium formation and its subsequent reaction with the oxyallene partners. This is our first success of leveraging the unique reactivity engendered by Pd–H species in concert with C1-ammonium enolate formation. In addition to greatly expanding the sphere of accessible reactivity, the efficiency of this two-catalyst construct processes raises the prospect of developing analogous stereodivergent reactions by judicious identification of chiral palladium catalysts compatible with this platform.[26]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Allenes · C1-Ammonium Enolates · Enantioselectivity · Isothioureas · Palladium Catalysis

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